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(54) **PROPYLENE POLYMERS INCORPORATING POLYETHYLENE MACROMERS**

PROPYLENPOLYMERE ENTHALTEND POLYETHYLENMAKROMONOMERE

POLYPROPYLENE RENFERMANT DES MACROMERES DE POLYETHYLENE

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Description

[0001] This application is based on U.S. provisional applications 60/037323, filed 2/7/97, 60/046812, filed 5/2/97, and 60/067782, filed 12/10/97,

FIELD OF THE INVENTION

[0002] The present invention relates to propylene polymers incorporating macromers and a method for the preparation of branched polypropylene utilizing chiral, stereorigid transition metal catalyst compounds.

BACKGROUND OF THE INVENTION

[0003] Polypropylene and related polymers are known to have low melt strength. This is a significant deficiency in key application areas such as thermoforming, blow molding, and fiber spinning. Polyethylene on the other hand is used extensively in blown film applications requiring good melt strength. The limitations in the melt strength of polypropylenes show up as excess sag in sheet extrusion, rapid thinning of walls in parts thermoformed in the melt phase, low draw-down ratios in extrusion coating, poor bubble formation in extrusion foam materials, and relative weakness in large-part blow molding. Thus, it would be highly desirable to produce polypropylene and related polymers having enhanced melt strength as well as commercially valuable processability.

[0004] Increasing the melt strength of polymers such as polypropylene has been an industrial goal for well over ten years, however, success has been limited. The desirable properties that have made low density polyethylene commercially successful are attributed in large part to high melt strength and excellent processability. Both of these properties are attributed to the presence of long chain branching which is thought to occur under high pressure polymerization conditions.

[0005] There has been some success in increasing the melt strength of polypropylene. For example, EP 190 889 A2 discloses high energy irradiation of polypropylene to create what is believed to be polypropylene having substantial free-end long branches of propylene units. EP 384 431 discloses the use of peroxide decomposition of polypropylene in the substantial absence of oxygen to obtain a similar product.

[0006] Other attempts to improve the melt properties of polypropylene include US Patent 5,541,236, which introduces long chain branching by bridging two PP backbones to form H-type polymers, and US Patent 5,514,761, which uses dienes incorporated in the backbones to achieve a similar effect. However, it is difficult to avoid cross-linking and gel formation in such processes.

[0007] Thus, there is still a need for propylene polymers having improved melt strength and good processability.

SUMMARY OF THE INVENTION

[0008] The present invention meets that need by providing a polyolefin product which comprises a branched olefin copolymer having a crystalline polypropylene backbone, polyethylene branches and, optionally, one or more comonomers present in said backbone, said branches, or both said backbone and said branches, wherein the total comonomer content of said branched olefin copolymer is from 0 to 20 mole percent, and further, wherein the mass ratio of said crystalline polypropylene to said polyethylene ranges from 99.9:0.1 to 50:50. Additionally, a process is provided for preparing a branched olefin copolymer comprising:

- a) copolymerizing ethylene, optionally with one or more copolymerizable monomers, in a polymerization reaction under conditions sufficient to form copolymer having greater than 40% chain end-group unsaturation;
- b) copolymerizing the product of a) with propylene and, optionally, one or more copolymerizable monomers, in a polymerization reactor under suitable polypropylene polymerization conditions using a chiral, stereorigid transition metal catalyst capable of producing crystalline polypropylene; and
- c) recovering a branched olefin copolymer.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009]

Figure 1 is a graphic illustration of the GPC-FTIR data for the polymer produced in Example 4.

Figure 2 is a graphic illustration of the complex viscosity vs. shear rate curve for the polymer products produced in Example 5 and Comparative Example 7

DETAILED DESCRIPTION OF THE INVENTION

[0010] The polyolefin compositions of this invention are comprised of branched polymers wherein the polymer backbone is derived from propylene and the polymer branches are derived from polyethylene. The branches and backbone are polymerized under coordination or insertion conditions with activated transition metal organometallic catalyst compounds. The branches are composed of polyethylene which may exhibit crystalline, semi-crystalline or glassy properties suitable for hard phase domains in accordance with the art understood meaning of those terms, and are attached to a polymeric backbone that is also crystalline. The backbone is composed of stereospecific polypropylene and, optionally, one or more comonomers. In addition, the backbone has a melt point of 80°C or higher. Preferably, the backbone is isotactic polypropylene. These compositions are useful as thermoforming resins and exhibit improved processability over current polypropylene compositions.

[0011] In the branched olefin copolymer of the present invention, the mass ratio of the isotactic polypropylene to the polyethylene ranges from 99.9:0.1 to 50:50. Preferably, the mass ratio of the isotactic polypropylene to the polyethylene ranges from 95:5 to 50:50.

[0012] As used herein, "isotactic polypropylene" is defined as having at least 70% isotactic pentads according to analysis by ¹³C-NMR. "Highly isotactic polypropylene" is defined as having at least 90% isotactic pentads according to analysis by ¹³C-NMR. "Syndiotactic polypropylene" is defined as polypropylene having at least 70% syndiotactic pentads according to analysis by ¹³C-NMR. Preferably, the backbone of the present invention is highly isotactic polypropylene.

The Macromer Sidechains

[0013] The branches of the polymer (also referred to as "sidechains") are comprised ethylene and, optionally, one or more comonomers. Preferably, the comonomers are chemical units capable of forming crystalline or glassy polymeric segments under conditions of insertion polymerization. Suitable comonomers include C₃-C₂₀ α-olefins, geminally disubstituted monomers, C₅-C₂₅ cyclic olefins, C₅-C₂₅ styrenic olefins and lower carbon number (C₃-C₈) alkyl-substituted analogs of the cyclic and styrenic olefins. Thus, typically, the branches can comprise from 85-100 mol% ethylene, and from 0-15 mol% comonomer, preferably 90 -99 mol% ethylene and 1-10 mol% comonomer, most preferably 94 -98 mol% ethylene and 2-6 mol% comonomer. In particular, as the sidechain Mn increases above about 3,000, it is preferable to introduce small amounts of comonomer to minimize embrittlement, e.g., about 0.2 - 4.0 mol.% comonomer. The selection of comonomer can be based upon properties other than crystallinity disrupting capability, for instance, a longer olefin comonomer, such as 1-octene, may be preferred over a shorter olefin such as 1-butene for improved polyethylene film tear. For improved polyethylene film elasticity or barrier properties, a cyclic comonomer such as norbornene or alkyl-substituted norbornene may be preferred over an α-olefin.

[0014] The sidechains can have narrow or broad molecular weight distribution (Mw/Mn), for example, from 1.1 to 30, typically 2-8. Additionally, the sidechains can have different comonomer compositions, e.g., including the orthogonal compositional distributions described in U.S. patent 5,382,630 (CDBI >50%), incorporated by reference for purposes of U. S. patent practice. Optionally, mixtures of sidechains with different molecular weights and/or compositions may be used.

[0015] The M_n of the sidechains are within the range of from greater than or equal to 500 and less than or equal to 45,000. Preferably the M_n of the sidechains is from 1500 to 30,000, and more preferably the M_n is from 1500 to 25,000. A preferred branched olefinic copolymer within this class will have a melt enthalpy (ΔH_m) as measured by differential scanning calorimetry of 90 cal/g (measured by integrating heat flows recorded at temperatures ≥ 80 °C while scanning at ≥ 5 °C/min).

[0016] Conditions sufficient to form the sidechain copolymer include using suitable ethylene and comonomer reactant ratios to assure the described sidechain olefin-derived unit constitution, plus catalyst and process conditions conducive to forming the unsaturated chain ends. The teachings of copending provisional application U.S. Ser. No. 60/037323 filed 02/07/97 are specific to suitable catalyst selection and use to prepare macromeric copolymer chains with a high yield of vinyl unsaturation. The metallocene catalyst used in the step a) preparation of the unsaturation-containing macromer can be essentially any catalyst capable of insertion polymerization of ethylene, it can be one capable of high comonomer incorporation capability (see below) or of low comonomer incorporation capability. Those of low incorporation capability are typically those that are more congested at the metal coordination site, thus unbridged and substituted unbridged metallocene catalysts are particularly suitable. See also the teachings of U.S. Patent 5,498,809 and international publications WO 94/19436 and WO 94/13715, describing means of preparing vinylidene-terminated ethylene-1-butene copolymers in high yields. See also, the teachings of copending application U.S. Ser. No. 08/651,030, filed 21 May 1996, as to the preparation of ethylene-isobutylene copolymers having high levels of vinylidene chain-end unsaturation. Throughout the description above, and below, the phrase "chain-end" or "terminal" when referring to unsaturation means olefin unsaturation suitable for insertion polymerization whether or not located precisely at the

terminus of a chain. All documents of this paragraph are incorporated by reference for purposes of U.S. patent practice.

[0017] In a particular embodiment, polymeric unsaturation-containing macromer product suitable as branches for a subsequent copolymerization reaction can be prepared under solution polymerization conditions with preferred molar ratios of aluminum in the alkyl alumoxane activator, e.g., methyl alumoxane (MAO), to transition metal. Preferably that level is ≥ 20 and ≤ 175 ; more preferably ≥ 20 and ≤ 140 ; and, most preferably ≥ 20 and ≤ 100 . The temperature, pressure and time of reaction depend upon the selected process but are generally within the normal ranges for a solution process. Thus temperatures can range from 20°C to 200°C, preferably from 30°C to 150°C, more preferably from 50°C to 140°C, and most preferably between 55°C and 135°C. The pressures of the reaction generally can vary from atmospheric to 345 MPa, preferably to 182 MPa. For typical solution reactions, temperatures will typically range from ambient to 250°C with pressures from ambient to 3.45 MPa. The reactions can be run batchwise. Conditions for suitable slurry-type reactions are similar to solution conditions except reaction temperatures are limited to those below the melt temperature of the polymer. In an additional, alternative reaction configuration, a supercritical fluid medium can be used with temperatures up to 250°C and pressures up to 345 MPa. Under high temperature and pressure reaction conditions, macromer product of lower molecular weight ranges are typically produced, e.g., M_n about 1,500.

[0018] Suitable catalyst compounds that when activated can achieve high chain-end unsaturations specifically include those identified above with respect to the preparation of high vinyl or vinylidene-containing macromers. Catalyst compounds which are suitable for preparing the branched olefin copolymer of the present invention are discussed in more detailed below.

[0019] The polyethylene macromers can have narrow or broad molecular weight distribution (M_w/M_n), for example, from 1.5 to 5, typically 1.7 to 3. Optionally, mixtures of sidechains with different molecular weights may be used.

[0020] Preferably, the macromers of the present invention are made using solution-phase conditions. Preferred solvents for solution phase reactions are selected on the basis of polymer solubility, volatility and safety/health considerations. Nonpolar alkanes or aromatics are preferred.

The Polyolefin Backbone

[0021] The polyolefin backbone of the present invention is composed of propylene monomers and, optionally, one or more comonomers. In one embodiment of the present invention, no comonomers are present in the polyolefin backbone, resulting in a polymer having an isotactic polypropylene backbone and polyethylene sidechains.

[0022] In another embodiment of the present invention, one or more comonomers are present in the backbone. Comonomers which are useful in the present invention include ethylene, C_4 - C_{20} α -olefins, and lower carbon number (C_3 - C_8) alkyl substituted analogs of the cyclic and styrenic olefins. Other copolymerizable monomers include geminally disubstituted olefins such as isobutylene, C_5 - C_{25} cyclic olefins such as cyclopentene, norbornene and alkyl-substituted norbornenes, and styrenic monomers such as styrene and alkyl substituted styrenes. Comonomers are selected for use based on the desired properties of the polymer product and the metallocene employed will be selected for its ability to incorporate the desired amount of olefins.

[0023] When comonomers are used, they preferably comprise from 3 to 20 mole percent of the branched olefin copolymer. More preferably, the comonomers comprise from 5 to 17 mole percent of the branched olefin copolymer.

[0024] In another embodiment of the present invention, the backbone of the present invention contains syndiotactic polypropylene and, optionally, one or more comonomers. Essentially all of the backbone can be syndiotactic, resulting in a polymer having a syndiotactic polypropylene backbone and polyethylene sidechains. Alternatively, the backbone can be a combination of syndiotactic and isotactic polypropylene with, optionally, one or more comonomers.

[0025] The mass of the backbone will typically comprise at least 40 wt% of the total polymer mass, that of the backbone and the sidechains together, so the backbone typically will have a nominal weight-average molecular weight (M_w) weight of at least equal to or greater than about 60,000. The term nominal is used to indicate that direct measurement of M_w of the backbone is largely impossible but that characterization of the copolymer product will exhibit measurements of M_w that correlate to a close approximate weight of the polymeric backbone inclusive only of the monoolefin mer derivatives and the insertion moieties of the sidebranches when the macromer consists of less than 50% of the total polymer mass.

Catalysts

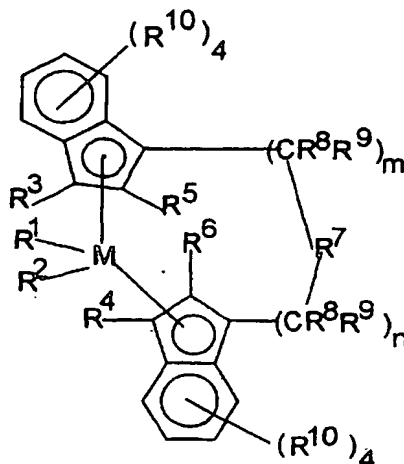
[0026] Catalysts which are useful for producing the branched polyolefin of the present invention include all catalysts which are capable of producing isotactic polypropylene and incorporating significant quantities of the isotactic polyethylene macromers of the present invention. Preferably, metallocene catalysts are used.

[0027] As used herein "metallocene" refers generally to compounds represented by the formula $Cp_mMR_nX_q$ wherein Cp is a cyclopentadienyl ring which may be substituted, or derivative thereof which may be substituted, M is a Group 4, 5, or 6 transition metal, for example titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molyb-

denum and tungsten, R is a hydrocarbonyl group or hydrocarboxy group having from one to 20 carbon atoms, X is a halogen, and $m=1-3$, $n=0-3$, $q=0-3$, and the sum of $m+n+q$ is equal to the oxidation state of the transition metal.

[0028] Methods for making and using metallocenes are well known in the art. For example, metallocenes are detailed in United States Patent Nos. 4,530,914; 4,542,199; 4,769,910; 4,808,561; 4,871,705; 4,933,403; 4,937,299; 5,017,714; 5,057,475; 5,120,867; 5,278,119; 5,304,614; 5,324,800; 5,350,723; 5,391,790; and 5,635,573 each fully incorporated herein by reference.

[0029] Preferred metallocenes are those that are stereorigid and comprise a Group 4, 5, or 6 transition metal, bis-cyclopentadienyl derivative, preferably bis-indenyl metallocene components having the following general structure:



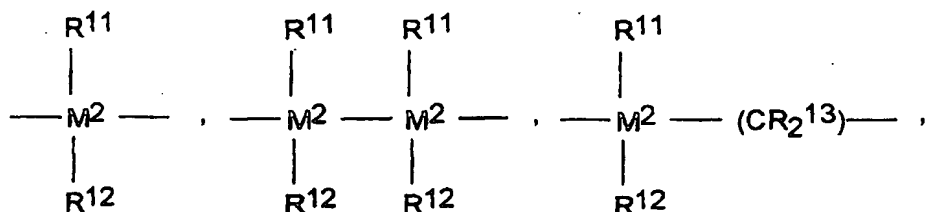
wherein M¹ is a metal of Group 4, 5, or 6 of the Periodic Table, for example titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten, preferably, zirconium, hafnium and titanium, most preferably zirconium and hafnium;

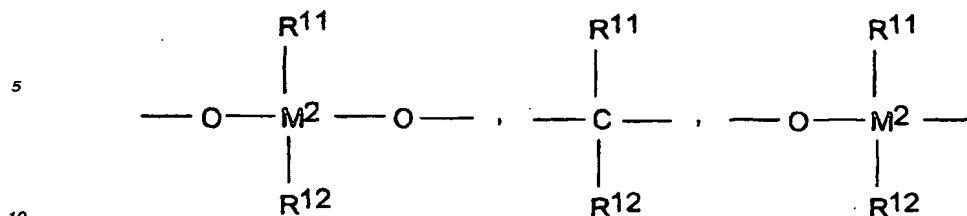
[0030] R¹ and R² are identical or different, are one of a hydrogen atom, a C₁-C₁₀ alkyl group, preferably a C₁-C₃ alkyl group, a C₁-C₁₀ alkoxy group, preferably a C₁-C₃ alkoxy group, a C₆-C₁₀ aryl group, preferably a C₆-C₈ aryl group, a C₆-C₁₀ aryloxy group, preferably a C₆-C₈ aryloxy group, a C₂-C₁₀ alkenyl group, preferably a C₂-C₄ alkenyl group, a C₇-C₄₀ arylalkyl group, preferably a C₇-C₁₀ arylalkyl group, a C₇-C₄₀ alkylaryl group, preferably a C₇-C₁₂ alkylaryl group, a C₈-C₄₀ arylalkenyl group, preferably a C₈-C₁₂ arylalkenyl group, or a halogen atom, preferably chlorine;

R³ and R⁴ are hydrogen atoms;

R⁵ and R⁶ are identical or different, preferably identical, are one of a hydrogen atom, halogen atom, preferably a fluorine, chlorine or bromine atom, a C₁-C₁₀ alkyl group, preferably a C₁-C₄ alkyl group, which may be halogenated, a C₆-C₁₀ aryl group, which may be halogenated, preferably a C₆-C₈ aryl group, a C₂-C₁₀ alkenyl group, preferably a C₂-C₄ alkenyl group, a C₇-C₄₀ arylalkyl group, preferably a C₇-C₁₀ arylalkyl group, a C₇-C₄₀ alkylaryl group, preferably a C₇-C₁₂ alkylaryl group, a C₈-C₄₀ arylalkenyl group, preferably a C₈-C₁₂ arylalkenyl group, a -NR₂¹⁵, -SR¹⁵, -OR¹⁵, -OSiR₃¹⁵ or -PR₂¹⁵ radical, wherein R¹⁵ is one of a halogen atom, preferably a chlorine atom, a C₁-C₁₀ alkyl group, preferably a C₁-C₃ alkyl group, or a C₆-C₁₀ aryl group, preferably a C₆-C₉ aryl group;

R⁷ is





=BR¹¹, =AIR¹¹, -Ge-, -Sn-, -O-, -S-, =SO, =SO₂, =NR¹¹, =CO, PR¹¹, or =P(O)R¹¹;
wherein:

15 R¹¹, R¹² and R¹³ are identical or different and are a hydrogen atom, a halogen atom, a C₁-C₂₀ alkyl group, preferably a C₁-C₁₀ alkyl group, a C₁-C₂₀ fluoroalkyl group, preferably a C₁-C₁₀ fluoroalkyl group, a C₆-C₃₀ aryl group, preferably a C₆-C₂₀ aryl group, a C₆-C₃₀ fluoroaryl group, preferably a C₆-C₂₀ fluoroaryl group, a C₁-C₂₀ alkoxy group, preferably a C₁-C₁₀ alkoxy group, a C₂-C₂₀ alkenyl group, preferably a C₂-C₁₀ alkenyl group, a C₇-C₄₀ arylalkyl group, preferably a C₇-C₂₀ arylalkyl group, a C₈-C₄₀ arylalkenyl group, preferably a C₈-C₂₂ arylalkenyl group, a C₇-C₄₀ alkylaryl group, preferably a C₇-C₂₀ alkylaryl group or R¹¹ and R¹², or R¹¹ and R¹³, together with the atoms binding them, can form ring systems;

M² is silicon, germanium or tin, preferably silicon or germanium, most preferably silicon;

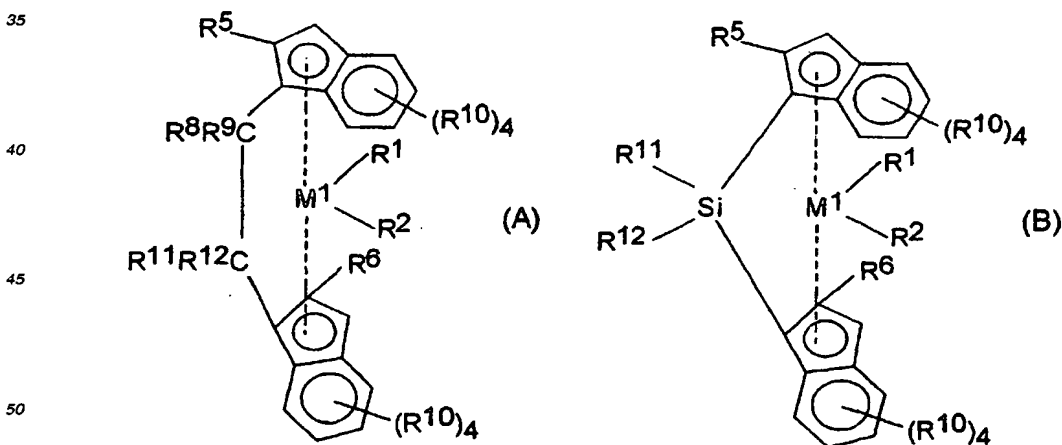
R⁸ and R⁹ are identical or different and have the meanings stated for R¹¹;

25 m and n are identical or different and are zero, 1 or 2, preferably zero or 1, m plus n being zero, 1 or 2, preferably zero or 1; and

the radicals R¹⁰ are identical or different and have the meanings stated for R¹¹, R¹² and R¹³. Two adjacent R¹⁰ radicals can be joined together to form a ring system, preferably a ring system containing from about 4-6 carbon atoms.

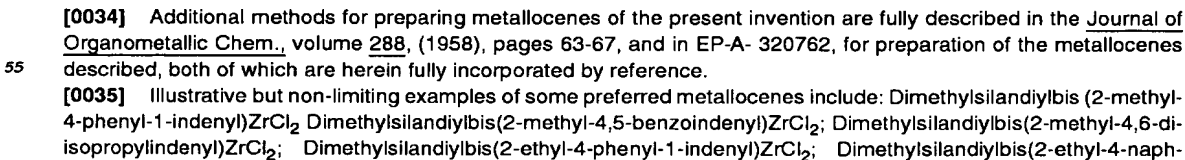
30 Alkyl refers to straight or branched chain substituents. Halogen (halogenated) is fluorine, chlorine, bromine or iodine atoms, preferably fluorine or chlorine.

[0031] Particularly preferred metallocenes are compounds of the structures:



wherein:

55 M¹ is Zr or Hf, R¹ and R² are methyl or chlorine, and R⁵, R⁶, R⁸, R⁹, R¹⁰, R¹¹ and R¹² have the above-mentioned meanings.



thyl-1-indenyl)ZrCl₂, Phenyl(Methyl)silandiylbis(2-methyl-4-phenyl-1-indenyl)ZrCl₂, Dimethylsilandiylbis(2-methyl-4-(1-naphthyl)-1-indenyl)ZrCl₂, Dimethylsilandiylbis(2-methyl-4-(2-naphthyl)-1-indenyl)ZrCl₂, Dimethylsilandiylbis(2-methyl-indenyl)ZrCl₂, Dimethylsilandiylbis(2-methyl-4,5-diisopropyl-1-indenyl)ZrCl₂, Dimethylsilandiylbis(2,4,6-trimethyl-1-indenyl)ZrCl₂, Phenyl(Methyl)silandiylbis(2-methyl-4,6-diisopropyl-1-indenyl)ZrCl₂, 1,2-Ethandiylbis(2-methyl-4,6-diisopropyl-1-indenyl)ZrCl₂, 1,2-Butandiylbis(2-methyl-4,6-diisopropyl-1-indenyl)ZrCl₂, Dimethylsilandiylbis(2-methyl-4-ethyl-1-indenyl)ZrCl₂, Dimethylsilandiylbis(2-methyl-4-isopropyl-1-indenyl)ZrCl₂, Dimethylsilandiylbis(2-methyl-4-t-butyl-1-indenyl)ZrCl₂, Phenyl(Methyl)silandiylbis(2-methyl-4-isopropyl-1-indenyl)ZrCl₂, Dimethylsilandiylbis(2-ethyl-4-methyl-1-indenyl)ZrCl₂, Dimethylsilandiylbis(2,4-dimethyl-1-indenyl)ZrCl₂, Dimethylsilandiylbis(2-methyl-4-ethyl-1-indenyl)ZrCl₂, Dimethylsilandiylbis(2-methyl- α -acenaphth-1-indenyl)ZrCl₂, Phenyl(Methyl)silandiylbis(2-methyl-4,5-benzo-1-indenyl)ZrCl₂, Phenyl(Methyl)silandiylbis(2-methyl-4,5-(methylbenzo)-1-indenyl)ZrCl₂, Phenyl(Methyl)silandiylbis(2-methyl-4,5-(tetramethylbenzo)-1-indenyl)ZrCl₂, Phenyl(Methyl)silandiylbis(2-methyl- α -acenaphth-1-indenyl)ZrCl₂, 1,2-Ethandiylbis(2-methyl-4,5-benzo-1-indenyl)ZrCl₂, 1,2-Butandiylbis(2-methyl-4,5-benzo-1-indenyl)ZrCl₂, Dimethylsilandiylbis(2-methyl-4,5-benzo-1-indenyl)ZrCl₂, 1,2-Ethandiylbis(2,4,7-trimethyl-1-indenyl)ZrCl₂, Dimethylsilandiylbis(2-methyl-1-indenyl)ZrCl₂, 1,2-Ethandiylbis(2-methyl-1-indenyl)ZrCl₂, Phenyl(Methyl)silandiylbis(2-methyl-1-indenyl)ZrCl₂, Diphenylsilandiylbis(2-methyl-1-indenyl)ZrCl₂, 1,2-Butandiylbis(2-methyl-1-indenyl)ZrCl₂, Dimethylsilandiylbis(2-ethyl-1-indenyl)ZrCl₂, Dimethylsilandiylbis(2-methyl-5-isobutyl-1-indenyl)ZrCl₂, Phenyl(Methyl)silandiylbis(2-methyl-5-isobutyl-1-indenyl)ZrCl₂, Dimethylsilandiylbis(2-methyl-5-t-butyl-1-indenyl)ZrCl₂, Dimethylsilandiylbis(2,5,6-trimethyl-1-indenyl)ZrCl₂, and the like.

[0036] Some preferred metallocene catalyst components are described in detail in U.S. Patent Nos. 5,149,819, 5,243,001, 5,239,022, 5,296,434 and 5,276,208 all of which are herein fully incorporated by reference. In addition, the bis-amido and bis-arylamido transition metal catalysts of U.S. patent 5,318,935 and copending U.S. patent application 08/ 803,687, filed 2/24/97, and the α -diimine nickel catalyst complexes of WO 96/23010 can be useful in incorporating the macromers of the present invention into the backbone.

[0037] Most preferably, the catalyst used to produce the branched polyolefin of the present invention is a dimethylsilyl-bridged bis-indenyl zirconocene or hafnocene such as dimethylsilyl bis(2-methyl-indenyl) ZrCl₂, dimethylsilyl bis(2-methyl-4-phenyl-1-indenyl) ZrCl₂, dimethylsilyl bis(2-methyl-4-(1-naphthyl)-1-indenyl) ZrCl₂, or dimethylsilyl bis(indenyl) hafnium dimethyl.

[0038] Preferably, the catalysts used to produce the syndiotactic polypropylene backbone of the present invention are those disclosed in U.S. Patents 4,892,851, 5,155,080, and 5,132,381, the disclosures of which are hereby incorporated by reference.

[0039] The terms "cocatalyst" and "activator" are used herein interchangeably and are defined to be any compound or component which can activate a bulky ligand transition metal compound or a metallocene, as defined above. Alumoxane may be used as an activator. There are a variety of methods for preparing alumoxane, non-limiting examples of which are described in U.S. Patent No. 4,665,208, 4,952,540, 5,091,352, 5,206,199, 5,204,419, 4,874,734, 4,924,018, 4,908,463, 4,968,827, 5,308,815, 5,329,032, 5,248,801, 5,235,081, 5,157,137, 5,103,031 and EP-A-0 561 476, EP-B1-0 279 586, EP-A-0 594-218 and WO 94/10180, each of which is fully incorporated herein by reference. It may be preferable to use a visually clear methylalumoxane. A cloudy or gelled alumoxane can be filtered to produce a clear solution or clear alumoxane can be decanted from the cloudy solution.

[0040] It is also within the scope of this invention to use ionizing activators, neutral or ionic, or compounds such as tri(n-butyl)ammonium tetrakis(pentafluorophenyl)boron, which ionize the neutral metallocene compound. Such ionizing compounds may contain an active proton, or some other cation associated with but not coordinated or only loosely coordinated to the remaining ion of the ionizing compound. Combinations of activators are also contemplated by the invention, for example, alumoxane and ionizing activators in combinations, see for example, WO 94/07928.

[0041] Descriptions of ionic catalysts for coordination polymerization comprised of metallocene cations activated by non-coordinating anions appear in the early work in EP-A-0 277 003, EP-A-0 277 004 and US patent 5,198,401 and WO-A-92/00333 (incorporated herein by reference). These teach a preferred method of preparation wherein metallocenes (bisCp and monoCp) are protonated by an anion precursor such that an alkyl/hydride group is abstracted from a transition metal to make it both cationic and charge-balanced by the non-coordinating anion.

[0042] The term "noncoordinating anion" means an anion which either does not coordinate to said cation or which is only weakly coordinated to said cation thereby remaining sufficiently labile to be displaced by a neutral Lewis base. "Compatible" noncoordinating anions are those which are not degraded to neutrality when the initially formed complex decomposes. Further, the anion will not transfer an anionic substituent or fragment to the cation so as to cause it to form a neutral four coordinate metallocene compound and a neutral by-product from the anion. Noncoordinating anions useful in accordance with this invention are those which are compatible, stabilize the metallocene cation in the sense of balancing its ionic charge in a +1 state, yet retain sufficient lability to permit displacement by an ethylenically or acetylenically unsaturated monomer during polymerization.

[0043] The use of ionizing ionic compounds not containing an active proton but capable of producing the both the active metallocene cation and an noncoordinating anion is also known. See, EP-A-0 426 637 and EP-A-0 573 403

(incorporated herein by reference). An additional method of making the ionic catalysts uses ionizing anion pre-cursors which are initially neutral Lewis acids but form the cation and anion upon ionizing reaction with the metallocene compounds, for example the use of tris(pentafluorophenyl) boron. See EP-A-0 520 732 (incorporated herein by reference). Ionic catalysts for addition polymerization can also be prepared by oxidation of the metal centers of transition metal compounds by anion pre-cursors containing metallic oxidizing groups along with the anion groups, see EP-A-0 495 375 (incorporated herein by reference).

[0044] Where the metal ligands include halogen moieties (for example, bis-cyclopentadienyl zirconium dichloride) which are not capable of ionizing abstraction under standard conditions, they can be converted via known alkylation reactions with organometallic compounds such as lithium or aluminum hydrides or alkyls, alkylalumoxanes, Grignard reagents, etc. See EP-A-0 500 944 and EP-A1-0 570 982 (incorporated herein by reference) for *in situ* processes describing the reaction of alkyl aluminum compounds with dihalo-substituted metallocene compounds prior to or with the addition of activating anionic compounds.

Support Materials

[0045] The metallocenes described herein are preferably supported using a porous particulate material, such as for example, talc, inorganic oxides, inorganic chlorides and resinous materials such as polyolefin or polymeric compounds.

[0046] The most preferred support materials are porous inorganic oxide materials, which include those from the Periodic Table of Elements of Groups 2, 3, 4, 5, 13 or 14 metal oxides. Silica, alumina, silica-alumina, and mixtures thereof are particularly preferred. Other inorganic oxides that may be employed either alone or in combination with the silica, alumina or silica-alumina are magnesia, titania, zirconia, and the like.

[0047] Preferably the support material is porous silica which has a surface area in the range of from about 10 to about 700 m²/g, a total pore volume in the range of from about 0.1 to about 4.0 cc/g and an average particle size in the range of from about 10 to about 500 μm. More preferably, the surface area is in the range of from about 50 to about 500 m²/g, the pore volume is in the range of from about 0.5 to about 3.5 cc/g and the average particle size is in the range of from about 20 to about 200 μm. Most preferably the surface area is in the range of from about 100 to about 400 m²/g, the pore volume is in the range of from about 0.8 to about 3.0 cc/g and the average particle size is in the range of from about 30 to about 100 μm. The average pore size of typical porous support materials is in the range of from about 10 to about 1000 Å. Preferably, a support material is used that has an average pore diameter of from about 50 to about 500 Å, and most preferably from about 75 to about 350 Å. It may be particularly desirable to dehydrate the silica at a temperature of from about 100°C to about 800°C anywhere from about 3 to about 24 hours.

[0048] The metallocenes, activator and support material may be combined in any number of ways. Suitable support techniques are described in U. S. Patent Nos. 4,808,561 and 4,701,432 (each fully incorporated herein by reference.). Preferably the metallocenes and activator are combined and their reaction product supported on the porous support material as described in U. S. Patent No. 5,240,894 and WO 94/ 28034, WO 96/00243, and WO 96/00245 (each fully incorporated herein by reference.) Alternatively, the metallocenes may be preactivated separately and then combined with the support material either separately or together. If the metallocenes are separately supported, then preferably, they are dried then combined as a powder before use in polymerization.

[0049] Regardless of whether the metallocene and activator are separately precontacted or whether the metallocene and activator are combined at once, the total volume of reaction solution applied to porous support is preferably less than about 4 times the total pore volume of the porous support, more preferably less than about 3 times the total pore volume of the porous support and even more preferably in the range of from more than about 1 to less than about 2.5 times the total pore volume of the porous support. Procedures for measuring the total pore volume of porous support are well known in the art. The preferred method is described in Volume 1, *Experimental Methods in Catalyst Research*, Academic Press, 1968, pages 67-96.

[0050] Methods of supporting ionic catalysts comprising metallocene cations and noncoordinating anions are described in WO 91/09882, WO 94/03506, WO 96/04319 and U.S. patent 5,643,847 (incorporated herein by reference). The methods generally comprise either physical adsorption on traditional polymeric or inorganic supports that have been largely dehydrated and dehydroxylated, or using neutral anion precursors that are sufficiently strong Lewis acids to activate retained hydroxy groups in silica containing inorganic oxide supports such that the Lewis acid becomes covalently bound and the hydrogen of the hydroxy group is available to protonate the metallocene compounds.

[0051] The supported catalyst system may be used directly in polymerization or the catalyst system may be prepolymerized using methods well known in the art. For details regarding prepolymerization, see United States Patent Nos. 4,923,833 and 4,921,825, EP 0 279 863 and EP 0 354 893 each of which is fully incorporated herein by reference.

Polymerization Processes

[0052] The branched polyolefin of the present invention may be produced using the catalysts described above in

any process including gas, slurry or solution phase or high pressure autoclave processes. (As used herein, unless differentiated, "polymerization" includes copolymerization and "monomer" includes comonomer.) Additionally, combinations of the above reactor types in multiple, series reactors and/or multiple reaction conditions and/or multiple catalyst configurations are explicitly intended. Preferably, a gas or slurry phase process is used, most preferably a bulk liquid propylene polymerization process is used.

[0053] In the preferred embodiment, this invention is directed toward the bulk liquid polymerization and copolymerization of propylene in a slurry or gas phase polymerization process, particularly a slurry polymerization process. Another embodiment involves copolymerization reactions of propylene with one or more comonomers. Such comonomers include alpha-olefin monomers having from 4 to 20 carbon atoms, preferably 4-12 carbon atoms, for example alpha-olefin comonomers of ethylene, butene-1, pentene-1, 4-methylpentene-1, hexene-1, octene-1, decene-1. Other suitable comonomers include geminally disubstituted monomers, C₃-C₂₅ cyclic olefins such as cyclopentene or norbornene, styrenic olefins such as styrene, and lower carbon number (C₃-C₈) alkyl substituted analogs of the cyclic and styrenic olefins. In addition, comonomers such as polar vinyl, diolefins such as dienes, for example, 1,3-butadiene, 1,4-hexadiene, norbornadiene or vinylnorbornene, acetylene and aldehyde monomers are suitable.

[0054] Typically in a gas phase polymerization process a continuous cycle is employed wherein one part of the cycle of a reactor, a cycling gas stream, otherwise known as a recycle stream or fluidizing medium, is heated in the reactor by the heat of polymerization. The recycle stream usually contains one or more monomers continuously cycled through a fluidized bed in the presence of a catalyst under reactive conditions. This heat is removed in another part of the cycle by a cooling system external to the reactor. The recycle stream is withdrawn from the fluidized bed and recycled back into the reactor. Simultaneously, polymer product is withdrawn from the reactor and new or fresh monomer is added to replace the polymerized monomer. (See for example U.S. Patent Nos. 4,543,399; 4,588,790; 5,028,670; 5,352,749; 5,405,922, and 5,436,304 all of which are fully incorporated herein by reference.)

[0055] A slurry polymerization process generally uses pressures in the range of from about 1 to about 500 atmospheres or even greater and temperatures in the range of from -60°C to about 280°C. In a slurry polymerization, a suspension of solid, particulate polymer is formed in a liquid or supercritical polymerization medium to which propylene and comonomers and often hydrogen along with catalyst are added. The liquid employed in the polymerization medium can be, for example, an alkane or a cycloalkane. The medium employed should be liquid under the conditions of polymerization and relatively inert such as hexane and isobutane. In the preferred embodiment, propylene serves as the polymerization diluent and the polymerization is carried out using a pressure of from about 200 kPa to about 7,000 kPa at a temperature in the range of from about 50°C to about 120°C.

[0056] The periods of time for each stage will depend upon the catalyst system, comonomer and reaction conditions. In general, propylene should be homopolymerized for a time period sufficient to yield a composition having from about 10 to about 90 weight percent homopolymer based on the total weight of the polymer, preferably from about 20 to about 80 weight percent, even more preferably from about 30 to about 70 homopolymer weight percent based on the total weight of the polymer.

[0057] The above-described temperatures, reaction times and other conditions are considered suitable polypropylene polymerization conditions for the purposes of this invention.

[0058] The polymerization may be conducted in batch or continuous mode and the entire polymerization may take place in one reactor or, preferably, the polymerization may be carried out in a series of reactors. If reactors in series are used, then the comonomer may be added to any reactor in the series, however, preferably, the comonomer is added to the second or subsequent reactor.

[0059] Hydrogen may be added to the polymerization system as a molecular weight regulator in the first and/or subsequent reactors depending upon the particular properties of the product desired and the specific metallocenes used. When metallocenes having different hydrogen responses are used, the addition of hydrogen will affect the molecular weight distribution of the polymer product accordingly. A preferred product form is to have the comonomer be present in the high molecular weight species of the total polymer composition to provide a favorable balance of good film stretchability without breaking, coupled with low extractables, low haze and good moisture barrier in the film. Accordingly in this preferred case, the same or lower levels of hydrogen are utilized during copolymerization as were used during polymerization in the second or subsequent reactor.

[0060] For both polyethylene macromer product and branched polyolefin preparation, it is known that many methods and permutations of the ordering of addition of macromer and monomer species to the reactor are possible, some more advantageous than others. For example, it is widely known in the art that preactivation of the metallocene with alumoxane before addition to a continuous solution-phase reactor yields higher activities than continuous addition of metallocene and activator in two separate streams. Furthermore, it may be advantageous to control precontacting time to maximize catalyst effectiveness, e.g., avoiding excessive aging of the activated catalyst composition.

[0061] It is preferable to use the polyethylene macromers such that they are promptly functionalized or copolymerized after being prepared. The highly reactive vinyl groups appear to be susceptible to by-product reactions with adventitious impurities and, even, dimerization or addition reactions with other unsaturated group-containing polymeric chains. Thus

maintaining in a cooled, inert environment after preparation and prompt subsequent use will optimize the effectiveness of the use of the polyethylene macromer product. A continuous process utilizing series reactors, or parallel reactors will thus be effective, the polyethylene macromer product being prepared in one and continuously introduced into the other.

INDUSTRIAL UTILITY

[0062] The branched polyolefin polymers of the present invention exhibit improved melt strength and shear thinning characteristics to standard propylene copolymers. This results in improved processability of the polymers, e.g. increased shear thinning and high output for a constant energy input. These characteristics will result in improved processing in blow molding and thermoforming operations. For example, in thermoforming operations sag will be decreased and power consumption will be lowered in the extruders.

[0063] In order that the invention may be more readily understood, reference is made to the following examples, which are intended to illustrate the invention but not to limit the scope thereof.

EXAMPLES

General

[0064] All polymerizations were performed in a 2-liter Zipperclave reactor equipped with a water jacket for temperature control. Liquids were measured into the reactor using calibrated sight glasses. High purity (>99.5%) toluene was purified by passing first through basic alumina activated at high temperature in nitrogen, followed by molecular sieve activated at high temperature in nitrogen. Polymerization grade ethylene was supplied directly in a nitrogen-jacketed line and used without further purification. Propylene was purified by passing through activated basic alumina and molecular sieves. Methylalumoxane (MAO, 10% in toluene) was received from Albemarle Inc. in stainless steel cylinders, divided into 1-liter glass containers, and stored in a laboratory glove-box at ambient temperature.

[0065] For the polymer synthesis, propylene was measured into the reactor through a calibrated container. To ensure the reaction medium was well-mixed, a flat-paddle stirrer rotating at 750 rpm was used.

Reactor Preparation

[0066] The reactor was first, cleaned by heating to 150 °C in toluene to dissolve any polymer residues, then cooled and drained. Next, the reactor was heated using jacket water at 110 °C and the reactor was purged with flowing nitrogen for a period of ~30 minutes. Before reaction, the reactor was further purged using 3 nitrogen pressurize/vent cycles (to 100 psi). The cycling served two purposes: (1) to thoroughly penetrate all dead ends such as pressure gauges to purge fugitive contaminants and (2) to pressure test the reactor.

Catalysts

[0067] All catalyst preparations were performed in an inert atmosphere with <1.5 ppm H₂O content. The catalyst system used in the synthesis of macromer was Cp₂ZrCl₂ activated with MAO. The catalyst systems used in the synthesis of branched olefin copolymer were dimethylsilyl bis(indenyl)hafnium dimethyl and dimethylsilyl bis(2-methyl indenyl) zirconium dichloride. The dimethylsilyl bis(indenyl)hafnium dimethyl was activated with [DMAH]⁺ [(C₆F₅)₄ B]⁻. The dimethylsilyl bis(2-methyl indenyl) zirconium dichloride was activated with MAO. To maximize solubility of the metallocene, toluene was used as a solvent. The catalyst was added to a stainless steel tube by pipette and transferred to the reactor.

Macromer synthesis - General:

[0068] Ethylene was added to the reactor as needed to maintain total system pressure at the reported levels (semi-batch operation). Ethylene flow rate was monitored using a Matheson mass flow meter (model number 8272-0424). To ensure the reaction medium was well-mixed, a flat-paddle stirrer rotating at 750 rpm was used.

Example 1

[0069] The reactor was simultaneously purged of nitrogen and pressure tested using two ethylene fill/purge cycles (to 300 psig). Then, the reactor pressure was raised to ~40 psi to maintain positive reactor pressure during setup operations. Jacket water temperature was set to 120°C and 1200 milliliters of toluene were added to the reactor. The

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stirrer was set to 750 rpm. Additional ethylene was added to maintain a positive reactor gauge pressure as gas phase ethylene was absorbed into solution. The system was allowed to reach a steady temperature. The ethylene pressure regulator was next set to 40 psig and ethylene was added to the system until a steady state was achieved as measured by zero ethylene uptake. The reactor was isolated and a pulse of toluene pressurized to 300 psig was used to force the catalyst solution from the addition tube into the reactor. The ethylene supply manifold was immediately opened to the reactor in order to maintain a constant reactor pressure as ethylene was consumed by reaction.

[0070] After 60 minutes of reaction, the reactor was isolated, cooled to room temperature and methanol was added to precipitate the macromer product. The yield was 48 g. The polymer product had an Mn of 7,500 and a vinyl end group percentage of 73.

Example 2

[0071] The reactor was simultaneously purged of nitrogen and pressure tested using two ethylene fill/purge cycles (to 300 psig). Then, the reactor pressure was raised to ~40 psi to maintain positive reactor pressure during setup operations. Jacket water temperature was set to 120°C and 1200 milliliters of toluene were added to the reactor. The stirrer was set to 750 rpm. Additional ethylene was added to maintain a positive reactor gauge pressure as gas phase ethylene was absorbed into solution. The system was allowed to reach a steady temperature. The ethylene pressure regulator was next set to 40 psig and ethylene was added to the system until a steady state was achieved as measured by zero ethylene uptake. The reactor was isolated and a pulse of toluene pressurized to 300 psig was used to force the catalyst solution from the addition tube into the reactor. The ethylene supply manifold was immediately opened to the reactor in order to maintain a constant reactor pressure as ethylene was consumed by reaction.

[0072] After 20 minutes of reaction, the reactor was isolated, cooled to room temperature and methanol was added to precipitate the macromer product. The yield was 23.3 g. The polymer product had an Mn of 4,300 and a vinyl end group percentage of 73.

Example 3

[0073] A 2-liter reactor was charged with toluene (1 L), propylene (150 mL), 10 g of the polyethylene macromer from Example 1 and Triisobutylaluminum (2.0 mL of 1M solution in toluene). The reactor was heated to 90°C and equilibrated for 5 min. Then 2 mg of dimethylsilyl bis(indenyl)hafnium dimethyl and 6 mg of [DMAH]⁺ [(C₆F₅)₄ B]⁻ in 5 mL of toluene were injected using a catalyst tube. After 15 min, the reactor was cooled to 25°C and vented. The polymer was collected by filtration and dried in air for 12 hours. Yield: 40 g.

Example 4

[0074] A 2-liter autoclave reactor was charged with toluene (1 L), propylene (150 mL), 10 g of the polyethylene macromer from Example 1 and Triisobutylaluminum (2.0 mL of 1M solution in toluene). The reactor was heated to 90°C and equilibrated for 5 min. Then 2 mg of dimethylsilyl bis(2-methyl indenyl) zirconium dichloride activated in 5 mL of toluene and 1 mL of MAO (10wt% in toluene) was injected using a catalyst tube. After 15 min, the reactor was cooled to 25°C and vented. The polymer was collected by filtration and dried in air for 12 hours. Yield: 40 g.

Example 5

[0075] A 2-liter autoclave reactor was charged with toluene (1 L), propylene (150 mL), 10 g of the polyethylene macromer from Example 2 and Triisobutylaluminum (2.0 mL of 1M solution in toluene). The reactor was heated to 50°C and equilibrated for 5 min. Then 2 mg of dimethylsilyl bis(2-methyl indenyl) zirconium dichloride activated in 5 mL of toluene and 1 mL of MAO (10wt% in toluene) was injected using a catalyst tube. After 15 min, the reactor was cooled to 25°C and vented. The polymer was collected by filtration and dried in air for 12 hours. Yield: 53 g.

Example 6

[0076] A 2-liter autoclave reactor was charged with toluene (1 L), propylene (150 mL), 5 g of the polyethylene macromer from Example 2 and Triisobutylaluminum (2.0 mL of 1M solution in toluene). The reactor was heated to 50°C and equilibrated for 5 min. Then 2 mg of dimethylsilyl bis(2-methyl indenyl) zirconium dichloride activated in 5 mL of toluene and 1 mL of MAO (10wt% in toluene) was injected using a catalyst tube. After 15 min, the reactor was cooled to 25°C and vented. The polymer was collected by filtration and dried in air for 12 hours.

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Yield: 51 g.

Comparative Example 7

[0077] A 2-liter reactor was charged with toluene (1 L), propylene (150 mL), and Triisobutylaluminum (2.0 mL of 1M solution in toluene). The reactor was heated to 50°C and equilibrated for 5 min. Then 2 mg of dimethylsilyl bis(2-methyl indenyl) zirconium dichloride activated in 5 mL of toluene and 1 mL of MAO (10wt% in toluene) was injected using a catalyst tube. After 15 min, the reactor was cooled to 25°C and vented. The polymer was collected by filtration and dried in air for 12 hours. Yield: 63 g.

Product Characterization

[0078] Some general characterization data for the polymers made in the Examples 3-6 and Comparative Example 7 are listed in Table 1. The polymer product samples were analyzed by gel permeation chromatography using a Waters 150C high temperature system equipped with a DRI Detector, Shodex AT-806MS column and operating at a system temperature of 145°C. The solvent used was 1,2,4-trichlorobenzene, from which polymer sample solutions of 1.5 mg/ml concentration were prepared for injection. The total solvent flow rate was 1 ml/minute and the injection size was 300 microliters. After elution of the polymer samples, the resulting chromatograms were analyzed using the Waters Expert Ease program to calculate the molecular weight distribution and one or more of M_n , M_w and M_z averages.

[0079] The melting point of the polymer product samples was determined on a DSC 2910 Differential Scanning Calorimeter (TA Instruments). The reported melting points were recorded at second melt with a temperature ramp of 10°C/min. "Wt. % C₂" indicates the percentage of polyethylene macromer (C₂) incorporated into the polymer samples which was determined by Analytical Composition Distribution Analysis.

Table 1

Physical Data Summary				
Example	Mw	MWD	Tm (°C)	Wt. % C ₂
3	76,278	2.07	127	4
4	53,844	2.37	148	9
5	164,394	4.62	147	10
6	138,267	3.78	149	3
Comp.7	154,267	1.68	149	0

[0080] Additional analysis was conducted on the polymer produced in Example 4 to determine the amount of branching and branch distribution. Since the ethylene contents at various molecular weight regions can be readily determined by FTIR, it is possible to quantify the incorporation of macromer and calculate LCB distribution. Shown in Figure 1 is the GPC-FTIR analysis for the polymer made in Example 4. The dots indicate the ethylene content measured by FTIR at different molecular weight along the GPC curve. Since the molecular weight (M_n) of the PE macromer is 7,500, the ethylene content detected at high molecular region clearly indicates the incorporation of macromer in the PP backbones. More importantly, it is possible to calculate the statistical LCB-distribution (also shown in Figure 1). Assuming that all macromers have the equal probability of incorporation (all macromers are equally spaced along the PP backbones), then, the number of long chain branches at certain molecular weight may be calculated according to the following equation:

$$\# \text{ of LCB/Chain} = \frac{(\text{MW of Polymer, DRI}) (\text{wt. fraction of PE})}{(\text{Mn of Macromer}) (1 - \text{wt. fraction of PE})}$$

[0081] Figure 2 shows a complex viscosity vs. shear rate curve for the polymers produced in Example 5 and Comparative Example 7. Example 5 demonstrates a steeper curve than Comparative Example 7. A steeper curve correlates to improved shear thinning performance as the viscosity reduces more rapidly at high shear rates. Therefore, the polymer product which was produced using macromers demonstrates improved processability over a polymer which was produced without the use of macromers.

[0082] While certain representative embodiments and details have been shown for the purposes of illustrating the invention, it will be apparent to those skilled in the art that various changes in the process and products disclosed

herein may be made without departing from the scope of the invention, which is defined in the appended claims.

Claims

1. A polyolefin comprising a branched olefin copolymer having a crystalline polypropylene backbone, polyethylene branches and, optionally, one or more comonomers present in said backbone, said branches, or both said backbone and said branches, wherein the total comonomer content of said branched olefin copolymer is from 0 to 20 mole percent, and further, wherein the mass ratio of said crystalline polypropylene to said polyethylene ranges from 99.9:0.1 to 50:50.
2. The polyolefin of claim 1 wherein the crystalline polypropylene is isotactic polypropylene.
3. The polyolefin of claim 1 wherein no comonomers are present in either said backbone or said branches.
4. The polyolefin of claim 1 wherein one or more comonomers are present in said backbone.
5. The polyolefin of claim 4 wherein said one or more comonomers are selected from the group consisting of ethylene, C₄ - C₂₀ α-olefins, geminally disubstituted monomers, C₅ - C₂₅ cyclic olefins, C₅ - C₂₅ styrenic olefins, and lower carbon number (C₃ - C₈) alkyl substituted analogs of the cyclic and styrenic olefins.
6. The polyolefin of claim 1 wherein one or more comonomers are present in said branches.
7. The polyolefin of claim 6 wherein said one or more comonomers are selected from the group consisting of C₃ - C₂₀ α-olefins, geminally disubstituted monomers, C₅ - C₂₅ cyclic olefins, C₅ - C₂₅ styrenic olefins, and lower carbon number (C₃ - C₈) alkyl substituted analogs of the cyclic and styrenic olefins.
8. The polyolefin of claim 1 wherein said one or more comonomers comprise from 3 to 20 mole percent of said branched olefin copolymer.
9. The polyolefin of claim 8 wherein said one or more comonomers comprise from 5 to 17 mole percent of said branched olefin copolymer.
10. The polyolefin of claim 1 wherein the mass ratio of said crystalline polypropylene to said polyethylene ranges from 95:5 to 50:50.
11. The polyolefin of claim 1 prepared by the process comprising:
 - a) copolymerizing ethylene, optionally with one or more copolymerizable monomers, in a polymerization reaction under conditions sufficient to form copolymer having greater than 40% chain end-group unsaturation;
 - b) copolymerizing the product of a) with propylene and, optionally, one or more copolymerizable monomers, in a polymerization reactor under suitable polypropylene polymerization conditions using a chiral, stereorigid transition metal catalyst capable of producing crystalline polypropylene; and
 - c) recovering said branched olefin copolymer.
12. The polyolefin of claim 11 wherein step a) is conducted by a solution process in which said ethylene and one or more copolymerizable monomers are contacted with a transition metal olefin polymerization catalyst activated by an alumoxane cocatalyst, the mole ratio of aluminum to transition metal being less than 220:1.
13. The polyolefin of claim 11 wherein step b) is conducted in a separate reaction by solution, slurry or gas phase polymerization.
14. The polyolefin of claim 11 wherein said chiral, stereorigid transition metal catalyst compound in step b) is activated by an alumoxane cocatalyst or non-coordinating anion precursor.
15. A process for preparing a branched olefin copolymer comprising:
 - a) copolymerizing ethylene, optionally with one or more copolymerizable monomers, in a polymerization re-

action under conditions sufficient to form copolymer having greater than 40% chain end-group unsaturation;
 b) copolymerizing the product of a) with propylene and, optionally, one or more copolymerizable monomers,
 in a polymerization reactor under suitable polypropylene polymerization conditions using a chiral, stereorigid
 transition metal catalyst capable of producing crystalline polypropylene; and
 c) recovering said branched olefin copolymer.

16. The process of claim 15 wherein step a) is conducted by a solution process in which said ethylene and one or more copolymerizable monomers are contacted with a transition metal olefin polymerization catalyst activated by an alumoxane cocatalyst, the mole ratio of aluminum to transition metal being less than 220:1.

17. The process of claim 15 wherein step b) is conducted in a separate reaction by solution, slurry or gas phase polymerization.

18. The process of claim 15 wherein said chiral, stereorigid transition metal catalyst compound in step b) is activated by an alumoxane cocatalyst or non-coordinating anion precursor.

Revendications

1. Polyoléfine comprenant un copolymère oléfinique ramifié ayant un squelette polypropylène cristallin, des ramifications polyéthylène et, facultativement, un ou plusieurs comonomères présents dans ledit squelette, dans lesdites ramifications, ou bien à la fois dans ledit squelette et lesdites ramifications, dans laquelle la teneur totale en comonomères dudit copolymère oléfinique ramifié est comprise dans l'intervalle de 0 à 20 % en moles, et en outre dans laquelle le rapport en masse dudit polypropylène cristallin audit polyéthylène est compris dans l'intervalle de 99,9:0,1 à 50:50.

2. Polyoléfine suivant la revendication 1, dans laquelle le polypropylène cristallin consiste en polypropylène isotactique.

3. Polyoléfine suivant la revendication 1, dans laquelle aucun comonomère n'est présent dans ledit squelette ou lesdites ramifications.

4. Polyoléfine suivant la revendication 1, dans laquelle un ou plusieurs comonomères sont présents dans ledit squelette.

5. Polyoléfine suivant la revendication 4, dans laquelle ledit ou lesdits comonomères sont choisis dans le groupe consistant en l'éthylène, des α -oléfines en C₄ à C₂₀, des monomères disubstitués de manière géminée, des oléfines cycliques en C₅ à C₂₅, des oléfines styréniques en C₅ à C₂₅ et des analogues, à substituants alkyle en C₃ à C₈, ayant de plus petits nombres d'atomes de carbone, des oléfines cycliques et styréniques.

6. Polyoléfine suivant la revendication 1, dans laquelle un ou plusieurs comonomères sont présents dans lesdites ramifications.

7. Polyoléfine suivant la revendication 6, dans laquelle ledit ou lesdits comonomères sont choisis dans le groupe consistant en des α -oléfines en C₃ à C₂₀, des monomères disubstitués de manière géminée, des oléfines cycliques en C₅ à C₂₅, des oléfines styréniques en C₅ à C₂₅ et des analogues, à substituants alkyle en C₃ à C₈, ayant de plus petits nombres d'atomes de carbone, des oléfines cycliques et styréniques.

8. Polyoléfine suivant la revendication 1, dans laquelle ledit ou lesdits comonomères représentent 3 à 20 % en moles dudit copolymère oléfinique ramifié.

9. Polyoléfine suivant la revendication 8, dans laquelle ledit ou lesdits comonomères représentent 5 à 17 % en moles dudit copolymère oléfinique ramifié.

10. Polyoléfine suivant la revendication 1, dans laquelle le rapport en masse dudit polypropylène cristallin audit polyéthylène est compris dans l'intervalle de 95:5 à 50:50.

11. Polyoléfine suivant la revendication 1, préparée par le procédé comprenant les étapes consistant :

- a) à copolymériser de l'éthylène, facultativement avec un ou plusieurs monomères copolymérisables, dans une réaction de polymérisation dans des conditions suffisantes pour former un copolymère ayant plus de 40 % d'insaturation de groupes terminaux de chaîne ;
- b) à copolymériser le produit de a) avec du propylène et, facultativement, un ou plusieurs monomères copolymérisables, dans un réacteur de polymérisation dans des conditions convenables de polymérisation du polypropylène en utilisant un catalyseur à base de métal de transition stéréorigide chiral capable de produire du polypropylène cristallin ; et
- c) à recueillir ledit copolymère oléfinique ramifié.
12. Polyoléfine suivant la revendication 11, dans laquelle l'étape a) est mise en oeuvre par un procédé en solution dans lequel ledit éthylène et un ou plusieurs monomères copolymérisables sont mis en contact avec un catalyseur à base de métal de transition pour la polymérisation d'oléfines, activé par un cocatalyseur du type alumoxane, le rapport molaire de l'aluminium au métal de transition étant inférieur à 220:1.
13. Polyoléfine suivant la revendication 11, dans laquelle l'étape b) est mise en oeuvre dans une réaction distincte par polymérisation en solution, en suspension ou en phase gazeuse.
14. Polyoléfine suivant la revendication 11, dans laquelle le composé servant de catalyseur à base de métal de transition stéréorigide chiral dans l'étape b) est activé par un cocatalyseur du type alumoxane ou un précurseur anionique non coordinant.
15. Procédé pour la préparation d'un copolymère oléfinique ramifié, comprenant les étapes consistant :
- a) à copolymériser de l'éthylène, facultativement avec un ou plusieurs monomères copolymérisables, dans une réaction de polymérisation dans des conditions suffisantes pour former un copolymère ayant plus de 40 % d'insaturation de groupes terminaux de chaîne ;
- b) à copolymériser le produit de a) avec du propylène et, facultativement, un ou plusieurs monomères copolymérisables, dans un réacteur de polymérisation dans des conditions convenables de polymérisation du polypropylène en utilisant un catalyseur à base de métal de transition stéréorigide chiral capable de produire du polypropylène cristallin ; et
- c) à recueillir ledit copolymère oléfinique ramifié.
16. Procédé suivant la revendication 15, dans lequel l'étape a) est mise en oeuvre par un procédé en solution dans lequel ledit éthylène et un ou plusieurs monomères copolymérisables sont mis en contact avec un catalyseur à base de métal de transition pour la polymérisation d'oléfines activé par un cocatalyseur du type alumoxane, le rapport molaire de l'aluminium au métal de transition étant inférieur à 220:1.
17. Procédé suivant la revendication 15, dans lequel l'étape b) est mise en oeuvre dans une réaction distincte par polymérisation en solution, en suspension ou en phase gazeuse.
18. Procédé suivant la revendication 15, dans lequel ledit composé servant de catalyseur à base de métal de transition stéréorigide chiral dans l'étape b) est activé par un cocatalyseur du type alumoxane ou un précurseur anionique non coordinant.

Patentansprüche

1. Polyolefin, das verzweigtes Olefincopolymer mit kristallinem Polypropylen Grundgerüst, Polyethylenverzweigungen und gegebenenfalls einem oder mehreren Comonomeren umfasst, die in dem Grundgerüst, den Verzweigungen oder sowohl in dem Grundgerüst als auch in den Verzweigungen vorhanden sind, wobei der gesamte Comonomergehalt des verzweigten Olefincopolymers 0 bis 20 Mol.% beträgt und ferner das Massenverhältnis von dem kristallinen Polypropylen zu dem Polyethylen im Bereich von 99,9:0,1 bis 50:50 beträgt.
2. Polyolefin nach Anspruch 1, bei dem das kristalline Polypropylen isotaktisches Polypropylen ist.
3. Polyolefin nach Anspruch 1, bei dem in dem Grundgerüst oder den Verzweigungen keine Comonomere vorhanden sind.

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4. Polyolefin nach Anspruch 1, bei dem in dem Grundgerüst ein oder mehrere Comonomere vorhanden ist bzw. sind.
5. Polyolefin nach Anspruch 4, bei dem ein oder mehrere Comonomere aus der Gruppe bestehend aus Ethylen, C₄-bis C₂₀- α -Olefinen, geminal disubstituierten Monomeren, cyclischen C₅-bis C₂₅-Olefinen, styrolischen C₅-bis C₂₅-Olefinen und mit Alkyl mit niederer Kohlenstoffzahl (C₃ bis C₈) substituierten Analoga der cyclischen und styrolischen Olefine ausgewählt sind.
6. Polyolefin nach Anspruch 1, bei dem in den Verzweigungen ein oder mehrere Comonomere vorhanden ist bzw. sind.
7. Polyolefin nach Anspruch 6, bei dem das eine oder die mehreren Comonomere ausgewählt ist bzw. sind aus der Gruppe bestehend aus C₃-bis C₂₀- α -Olefinen, geminal disubstituierten Monomeren, cyclischen C₅-bis C₂₅-Olefinen, styrolischen C₅-bis C₂₅-Olefinen und mit Alkyl mit niederer Kohlenstoffzahl (C₃ bis C₈) substituierten Analoga der cyclischen und styrolischen Olefine.
8. Polyolefin nach Anspruch 1, bei dem das eine oder die mehreren Comonomere 3 bis 20 Mol.% des verzweigten Olefincopolymers umfasst bzw. umfassen.
9. Polyolefin nach Anspruch 8, bei dem das eine oder die mehreren Comonomere 5 bis 17 Mol.% des verzweigten Olefincopolymers umfasst bzw. umfassen.
10. Polyolefin nach Anspruch 1, bei dem das Massenverhältnis des kristallinen Polypropylens zu dem Polyethylen im Bereich von 95:5 bis 50:50 liegt.
11. Polyolefin nach Anspruch 1, das hergestellt ist nach dem Verfahren, das umfasst:
- a) Copolymerisieren von Ethylen, gegebenenfalls mit einem oder mehreren copolymerisierbaren Monomeren, in einer Polymerisationsreaktion unter Bedingungen, die ausreichend sind, um Copolymer mit mehr als 40 % Kettenendgruppenungesättigtheit zu bilden;
 - b) Copolymerisieren des Produkts von a) mit Propylen und gegebenenfalls einem oder mehreren copolymerisierbaren Monomeren in einem Polymerisationsreaktor unter geeigneten Polypropylenpolymerisationsbedingungen unter Verwendung eines chiralen, stereostarren Übergangsmetallkatalysators, der in der Lage ist, kristallines Polypropylen zu produzieren, und
 - c) Gewinnen des verzweigten Olefincopolymers.
12. Polyolefin nach Anspruch 11, bei dem Stufe a) nach einem Lösungsverfahren durchgeführt wird, bei dem das Ethylen und ein oder mehrere copolymerisierbaren Monomere mit Übergangsmetall-Olefinpolymerisationskatalysator kontaktiert werden, der durch Alumoxan-Cokatalysator aktiviert ist, wobei das Molverhältnis von Aluminium zu Übergangsmetall kleiner als 220:1 ist.
13. Polyolefin nach Anspruch 11, bei dem Stufe b) in einer separaten Reaktion durch Lösungs-, Aufschlämmungs- oder Gasphasenpolymerisation durchgeführt wird.
14. Polyolefin nach Anspruch 11, bei dem die chirale, stereostarre Übergangsmetallkatalysatorkomponente in Stufe b) durch Alumoxan-cokatalysator oder nicht-koordinierenden Anionvorläufer aktiviert wird.
15. Verfahren zur Herstellung von verzweigtem Olefincopolymer, umfassend:
- a) Copolymerisieren von Ethylen, gegebenenfalls mit einem oder mehreren copolymerisierbaren Monomeren, in einer Polymerisationsreaktion unter ausreichenden Bedingungen, um Copolymer mit mehr als 40 % Kettenendgruppenungesättigtheit zu bilden;
 - b) Copolymerisieren des Produkts von a) mit Propylen und gegebenenfalls einem oder mehreren copolymerisierbaren Monomeren in einem Polymerisationsreaktor unter geeigneten Polypropylenpolymerisationsbedingungen unter Verwendung eines chiralen, stereostarren Übergangsmetallkatalysators, der in der Lage ist, kristallines Polypropylen zu produzieren, und
 - c) Gewinnen des verzweigten Olefincopolymers.
16. Verfahren nach Anspruch 15, bei dem Stufe a) nach einem Lösungsverfahren durchgeführt wird, bei dem das

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Ethylen und ein oder mehrere copolymerisierbaren Monomere mit Übergangsmetall-Olefinpolymerisationskatalysator kontaktiert werden, der durch Alumoxan-Cokatalysator aktiviert ist, wobei das Molverhältnis von Aluminium zu Übergangsmetall kleiner als 220:1 ist.

- 5 17. Verfahren nach Anspruch 15, bei dem Stufe b) in einer separaten Reaktion durch Lösungs-, Aufschlammungs- oder Gasphasenpolymerisation durchgeführt wird.
18. Polyolefin nach Anspruch 15, bei dem die chirale, stereostarre Übergangsmetallkatalysatorverbindung in Stufe b) durch Alumoxancokatalysator oder nicht-kordinierenden Anionvorläufer aktiviert wird.
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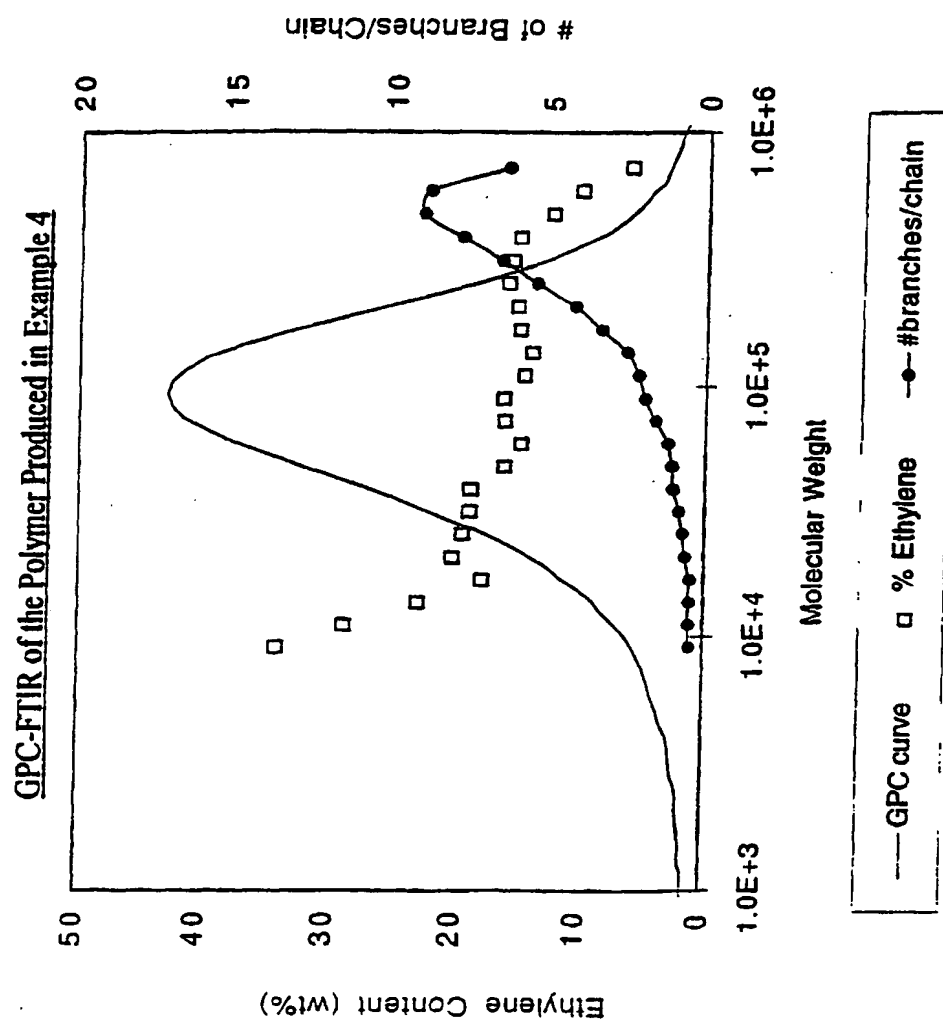
Fig. 1

Fig. 2

Complex Viscosity vs. Shear Rate

